

## PATENT ABSTRACTS OF JAPAN

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(54) PHOTOSEMICONDUCTOR ELECTRODEPOTOELECTRIC CONVERSION DEVICE AND  
POTOELECTRIC CONVERSION METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a photosemiconductor electrode efficiently usable of solar light and superior in photoelectric conversion efficiency, stability and durability by providing a layer having a perylene derivative represented by a specified formula adsorbed thereto on the base material surface of a metal oxide semiconductor.

SOLUTION: This photosemiconductor electrode has a layer having at least a perylene derivative represented by the formula I adsorbed thereto on the base material surface of a metal oxide semiconductor. In the formula R represents a divalent hydrocarbon group or a heterocyclic group which may be substituted. Examples of the metal oxide semiconductor include titanium oxide, tin oxide, tungsten oxide, zinc oxide, indium oxide, niobium oxide, strontium titanate and the like. They may be used alone as a single kind or in combination of two or more kinds thereof. Titanium oxide is particularly preferred from the viewpoint of photoelectric conversion characteristic, chemical stability, ease of manufacture and the like. The form, structure and size of the base material are not particularly limited and can be freely selected according to the purpose.

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CLAIMS

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[Claim(s)]

[Claim 1] An optical semiconductor electrode having the layer to which a perylene derivative expressed with following general formula (I) to a base material surface of a metal oxide semiconductor at least was made to stick.

General formula (I)

[Formula 1]

R expresses the divalent hydrocarbon group or heterocycle group which may be replaced among general formula (I).

[Claim 2] The optical semiconductor electrode according to claim 1 whose perylene derivative expressed with general formula (I) is a compound expressed with either following general formula (II) and (III).

General formula (II)

[Formula 2]

n expresses the integer of 1-20 among general formula (II).

General formula (III) [Formula 3]

X express a hydrogen atom a halogen atom  $\text{-CH}_3\text{-C}_2\text{H}_5\text{-OH-OCH}_3\text{-OCH}_3\text{-OC}_2\text{H}_5\text{-NH}_2\text{-COOH}$  or  $\text{-NO}_2$  among general formula (III). m and n express an integer of 0-3 respectively.

[Claim 3] The optical semiconductor electrode according to claim 1 or 2 in which a metal oxide semiconductor is chosen from titanium oxide, tin oxide, tungsten oxide, zinc oxide, indium oxide, niobium oxide and strontium titanate.

[Claim 4] The optical semiconductor electrode according to claim 1 or 2 whose metal oxide semiconductor is titanium oxide.

[Claim 5] A photoelectric conversion device which has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solution and an electrode of this couple so that energization is possible and is characterized by one side of an electrode of this couple being the optical semiconductor electrode according to any one of claims 1 to 4.

[Claim 6] In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solution and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this

coupleA photoelectric conversion methodwherein an electrode which irradiates with said light is the optical semiconductor electrode according to any one of claims 1 to 4.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the optical semiconductor electrode to which the specific perylene derivative was made to stick on the surface of a metal oxide semiconductorthe photoelectric conversion device using itand the photoelectric conversion method.

[0002]

[Description of the Prior Art]In recent yearsuse of sunlight attracts attention as an energy resource replaced with fossil fuelsuch as petroleum and coal. As a photoelectric conversion device which transforms light energy into electrical energy directlythe dry type solar cell in which p-n junction was formed on inorganic semiconductorssuch as silicon and gallium arsenideis known widelyand it is already put in practical use as a power supply of the object for remote placesor a portable electronic deviceetc. Howeversince the energy and cost which the manufacture takes are very high in the case of said dry type solar cellthere is a problem that it is difficult to use widely.

[0003]The wet solar cell whichon the other handused the

photoelectrochemical reaction which occurs by the interface of a semiconductor and an electrolytic solution as another photoelectric conversion device which transforms light energy into electrical energy is known. Metal oxide semiconductors used in said wet solar cellsuch as titanium oxide and tin oxideAs compared with the silicon used in said dry type solar cellgallium arsenideetc.it can manufacture at far low energy and costand titanium oxide is especially expected as a future energy conversion material from excelling in both sides of a photoelectric transfer characteristic and stability. Howeverit cannot be said that they can use only the ultraviolet radiation which is about 4% of sunlightbut their conversion efficiency is high enough since stable optical semiconductorssuch as titanium oxidehave the band gap as large as not less than 3 eV.

[0004]On the surface of this optical semiconductoras sensitizing dye Thenorganic coloring mattersuch as cyanine dye and a xanthene dyeTo make

organometallic complexessuch as a tris(2,2'-bipyridyl) ruthenium (II) complexadsorb and to carry out spectral sensitization is triedit is known that it is a method effective in improvement in conversion efficiency (T. -- OsaM. FujihiraNature. and 264349 (1976).) Brian O'ReganMichael GratzelNature353736 (1991)JP1-220380Aetc.

[0005]Howeverorganic coloring mattersuch as cyanine dye and a xanthene dyeis not enough in respect of stabilityenduranceetc. and on the other handalthough organometallic complexessuch as an organic ruthenium complexare excellent in fieldssuch as conversion efficiency and stabilitythere is a problem of being expensive. Thereforethe actual condition is efficient and that the cheap photoelectric conversion device is not yet provided by high durability.

[0006]

[Problem(s) to be Solved by the Invention]This invention solves many problems in said formerand makes it a technical problem to attain the following purposes. That isan object of this invention is to provide the optical semiconductor electrodephotoelectric conversion deviceand the photoelectric conversion method of it being efficiently availableand excelling in photoelectric conversion efficiencystabilityenduranceetc. and manufacturing sunlight cheaply and easily.

[0007]

[Means for Solving the Problem]

It is an optical semiconductor electrode having the layer to which a perylene derivative expressed with following general formula (I) to a base material surface of <1> metal oxide semiconductor at least was made to stick.

General formula (I)

[0008]

[Formula 4]

[0009]R expresses the divalent hydrocarbon group or heterocycle group which may be replaced among general formula (I).

The perylene derivative expressed with <2> general-formula (I) is an optical semiconductor electrode given in the above <1> which is a compound expressed with either following general formula (II) and (III). General formula (II)

[0010]

[Formula 5]

[0011]n expresses the integer of 1-20 among general formula (II).

General formula (III) [0012]

[Formula 6]

[0013]X express a hydrogen atom a halogen atom-CH<sub>3</sub>-C<sub>2</sub>H<sub>5</sub>-OH-OCH<sub>3</sub>-OCH<sub>3</sub>-OC<sub>2</sub>H<sub>5</sub>-NH<sub>2</sub>-COOH or -NO<sub>2</sub> among general formula (III). m and n express the integer of 0-3 respectively.

<3> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> chosen from titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide and strontium titanate.

<4> metal oxide semiconductors are optical semiconductor electrodes given in the above <1> or <2> which is titanium oxide.

It has at least a connecting means which connects the electrode of the couple immersed into <5> electrolytic solutions and the electrode of this couple so that energization is possible and one side of the electrode of this couple is a photoelectric conversion device characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.

<6> In a photoelectric conversion method of making an electrode of a couple mutually connected so that energization was possible immersed into an electrolytic solution and producing a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. An electrode which irradiates with said light is the photoelectric conversion method characterized by being an optical semiconductor electrode of a statement from the above <1> at either of <4>.

[0014] (Optical semiconductor electrode) An optical semiconductor electrode of this invention has the layer which made a perylene derivative stick to a base material surface of a metal oxide semiconductor at least.

[0015]- Substrate of a metal oxide semiconductor - As said metal oxide semiconductor, titanium oxide, tin oxide, tungstic oxide, zinc oxide, indium oxide, niobium oxide, strontium titanate etc. are mentioned for example. These may be used by an one-sort independent and may use two or more sorts together. Especially in this invention, reasons of a photoelectric transfer characteristic, chemical stability, manufacture ease etc. to titanium oxide is preferred also in these. There is no restriction in particular about shape of a substrate of said metal oxide semiconductor, structure and a size and it can choose suitably according to

the purpose. For example it may be a substrate which consists only of metal oxide semiconductors and may be a substrate which forms coating membrane of a metal oxide semiconductor on an electrode with publicly known tabular [ by a transparent electrode by ITO glass, silver glass etc., platinum, copper, black lead etc. ] or mesh state electrode etc. In the case of the latter substrate this coating membrane may be provided the whole surface on said publicly known electrode and may be provided in part.

[0016]- As a perylene derivative in perylene derivative-this invention what is expressed with said general formula (I) is mentioned suitably. In this invention a compound expressed with either said general formula (II) and (III) is preferred in a perylene derivative expressed with said general formula (I) and a compound specifically expressed with following formula (1) - (14) also in it is more preferred.

[0017]

[Formula 7]

[0018]

[Formula 8]

[0019] The perylene derivative shown by said general formula (I) For example it is obtained by making a 3,4,9,10-perylene tetracarboxylic anhydride and a general formula and the diamine compound (R expresses among a formula the divalent hydrocarbon group or heterocycle group which may be replaced.) expressed with  $H_2N-R-NH_2$  react. Although said at least 2 Eq (2 Eq or more) of diamine compounds are used to a 3,4,9,10-perylene tetracarboxylic anhydride on the occasion of said reaction In order to control the byproduction of polymer or oligomer it is preferred to use 10 Eq or more preferably [ using an excessive quantity as much as possible ] and generally.

[0020] A perylene derivative expressed with said general formula (I) is easily obtained using a cheap raw material and moreover is excellent in chemical stability, endurance etc. and is excellent in holdout in a base material surface of said metal oxide semiconductor and can carry out spectral sensitization of the optical semiconductor electrode stability and efficient over a long period of time.

[0021] (Production of an optical semiconductor electrode) A process of providing coating membrane to which a perylene derivative expressed with said general formula (I) was made sticking in a base material surface of

said metal oxide semiconductorIt is easily attained by immersing a substrate of said metal oxide semiconductor into a solution which dissolved with acid a perylene derivative expressed with this general formula (I) in a solvent.

[0022]What can form a salt of a perylene derivative and fusibility which are expressed with said general formula (I)ssuch as organic acidsuch as inorganic acidsuch as chloridesulfuric acidand phosphoric acidacetic acidbenzoic acidtrifluoroacetic acidtoluenesulfonic acidas said acidfor example is mentioned. These may be used by an one-sort independent and may use two or more sorts together. Also in thesewhen combination with the below-mentioned alcoholic solvent is taken into considerationespecially acetic acid is preferred.

[0023]As said solventpolar aprotic solventssuch as ketone solvents such as alcoholic solvents such as methanol and isopropyl alcoholacetoneand methyl ethyl ketonedimethyl sulfoxideand N,N-dimethylformamidewaterthese mixed solventsetc. are mentionedfor example. These may be used by an one-sort independent and may use two or more sorts together. Also in theseespecially alcoholic solvent is preferred.

[0024]Although content of a perylene derivative expressed with said general formula (I) in said solution can be suitably chosen according to the purpose processing condition etc.generally it is about 0.01-1 weight section to said solvent 100 weight section. Since content of said acid in said solution changes with sizes of a substrate of said metal oxide semiconductor etc. according to the purposecan choose suitablybut. At least two or more mol equivalents are required to said 1 mol of perylene derivativesandgenerally they are about 0.1-10 weight sections to said solvent 100 weight section.

[0025]It may carry out by heating to temperature below the boiling point of said solvent if needed in order to perform said immersion at a room temperature or to promote adsorption. After performing said immersionan optical semiconductor electrode of a request which washed a substrate of said metal oxide semiconductor using water or alcoholic solvent preferably and for which a layer to which a perylene derivative expressed with said general formula (I) sticks was formed in the surface arbitrary solvents and by drying is obtained. An optical semiconductor electrode of this invention produced by making it above can be used conveniently for the following photoelectric conversion devices and photoelectric conversion methods of this invention.

[0026] (Photoelectric conversion device) A photoelectric conversion device of this invention has at least a connecting means which connects an electrode of a couple immersed into an electrolytic solutionand an

electrode of this couple so that energization is possible. Said photoelectric conversion device may be provided with apparatus suitably selected according to the purpose etc. outside an electrode of said couple and said connecting means.

[0027]-A pair of electrodes - One side in an electrode of said couple is an optical semiconductor electrode of said this invention and another side is a counterelectrode. As said counterelectrode if electrochemically stable there will be no restriction in particular and according to the purpose it can choose from a publicly known thing suitably for example can choose from transparent electrodes such as flat electrodes such as platinum, gold and black lead or ITO glass and Nesa glass etc. suitably according to the purpose.

[0028]- Connecting means - As long as it has a function in which an electrode of said couple can be connected as said connecting means so that energization is possible there is no restriction in particular and can choose suitably according to the purpose but. For example a wire rod which consists of conductive materials such as a publicly known lead, various metal, carbon and a metallic oxide in itself, a plate, a printed film or a vacuum evaporation film is mentioned. This connecting means is connected to an electrode of said couple so that energization is possible. A photoelectric conversion device of the above this invention can be used conveniently for a photoelectric conversion method of the following this inventions.

[0029] (A photoelectric conversion method) A photoelectric conversion method of this invention makes an electrolytic solution immerse an electrode of a couple mutually connected so that energization was possible and produces a photoelectric conversion reaction by irradiating at least one side of an electrode of this couple. Those in an electrode of said couple who irradiate with light are the optical semiconductor electrodes of said this invention and another side is said counterelectrode. Said connecting means can be used for connecting an electrode of this couple so that energization is possible. For this reason as an electrode of said couple mutually connected so that energization was possible a photoelectric conversion device of said this invention can be used.

[0030]- Electrolytic solution - Although there is no restriction in particular and it can choose suitably as said electrolytic solution For examples salt such as potassium chloride, a lithium chloride, potassium carbonate and tetraethylammonium perchlorate. Nonaqueous solvent solution such as solutions such as acids such as alkalis such as sodium hydroxide and potassium carbonate, sulfuric acid and chloride and these



mixtures or alcohol and propylene carbonate etc. are mentioned. These may be used by an one-sort independent and may use two or more sorts together. In this invention a redox reagent from which it is the purpose of attaining stabilization of the photoelectric current characteristic and also potassium iodide-p-benzoquinone etc. produce an oxidation-reduction reaction reversibly may be added to said electrolytic solution.

[0031] (Photoelectric conversion reaction) In a photoelectric conversion device and a photoelectric conversion method of this invention a photoelectric conversion reaction can be produced as follows. That is an above-mentioned electrode i.e. said optical semiconductor electrode and said counter electrode of a couple are first immersed into said nature solution of an electric field. Next this optical semiconductor electrode is irradiated with monochromatic light of a 300-650-nm wavelength band white light which includes one in this wavelength band of zone or multicolor light. Then light energy is transformed into electrical energy in this optical semiconductor electrode. At this time it is changed into electrical energy very efficiently to light energy of visible light of not only ultraviolet radiation of a wavelength band below 300-400 nm but a 400-650-nm wavelength band.

[0032] Even visible light which cannot be used with metallic-oxide independent such as titanium oxide by using said optical semiconductor electrode in this invention can use effectively. As a result synthetic use of light such as sunlight is attained and light energy such as sunlight can be transformed into electrical energy at high efficiency. And in said optical semiconductor electrode to be used since coloring matter of a perylene derivative stuck to the surface firmly and has combined with it and it is not easily desorbed from this optical semiconductor electrode the characteristic of this optical semiconductor electrode is stabilized for a long period of time can be maintained and can always perform a photoelectric conversion reaction efficiently.

[0033]

[Example] Hereafter although the example of this invention is described this invention is not limited to these examples at all.

[0034] (Example 1)

- 25 ml of production-alt. titanate acid tetraisopropyl of the optical semiconductor electrode was gradually added into the mixed solution of 150 ml of pure water and the concentrated nitric acid 1.54g (specific gravity: 1.38) agitating violently. Temperature up was carried out to 80 °C. Continuing churning further more churning was continued at the temperature for 8 hours and the milky stable titanium oxide colloidal

solution was obtained. This colloidal solution was condensed to 40 ml at 30 \*\* under decompression of 30mmHg and the titanium oxide colloidal solution was prepared. Said titanium oxide colloidal solution was coated with the spin coat method on ITO/glass base material as an electrode and was calcinated at 500 \*\* for 1 hour. This operation was repeated 3 times and the titanium oxide enveloping layer about 1.0 micrometer thick was formed on this ITO/glass base material. When the crystal structure of the obtained layer was checked with the X-ray diffraction method it was checked that it is a mixture of an anatase and a rutile type. ITO/glass base material in which said titanium oxide enveloping layer was formed After 100 mg of NN'-bis(6'-amino-1'-hexyl)-3,4,9,10-perylene diimide tetracarboxylic acid (compound expressed above (5)) and 1 ml of glacial acetic acid are immersed in the solution which dissolved in 50 ml of methanol for 1 hour water washes Subsequently natural seasoning was washed and carried out with methanol.

[0035] Then the lead 7 was connected on the ITO film with which titanium oxide membrane is not covered the substrate end and the terminal area of the lead 7 were covered with the epoxy resin and the optical semiconductor electrode as shown in drawing 1 was produced. the optical semiconductor electrode 1 shown in drawing 1 -- the glass base material 2 top -- the ITO layer 3 and the titanium oxide layer 4 -- and The pigment layer 5 by NN'-bis(6'-amino-1'-hexyl)-3,4,9,10-perylene diimide tetracarboxylic acid (compound expressed above (5)) is laminated in this order The end of these lamination sides and the terminal area with the lead 7 were covered with the epoxy resin as the adhesive agent 6 and have adhered with it.

[0036]- The optical semiconductor electrode 1 produced as mentioned above as shown in production-drawing 2 of a photoelectric conversion device The platinum electrode selected as the counter electrode 9 and the saturation Calomel electrode selected as the reference electrode 10 were immersed in the electrolytic solution 11 in the transparent glass cell 13 each electrode was connected to the potentiostat 12 using the lead 7 as a connecting means and the photoelectric conversion device was produced. As said electrolytic solution 11 0.1M sodium sulfate / 0.02M potassium iodide solution was used. The lead 7 is connected to each electrode and energization has become possible. The lead 7 is accommodated in the glass tube 8. As the reference electrode 10 this photoelectric conversion device is equipped with the saturated calomel electrode so that energization is possible. The photoelectric conversion device was produced by the above.

[0037]- holding in the photoelectric conversion device obtained by more

than photoelectric conversion reaction --so that the potential of said optical semiconductor electrode may be set to 0V to said reference electrode -- white light (the xenon lamp of 500W.) It irradiated with illumination 4000lux or 550-nm monochromatic light (1 mW/cm<sup>2</sup>) from the back side of said optical semiconductor electrode. The value of the photoelectric current by the photoelectric conversion reaction produced at this time was measured with the potentiostat. The measurement result was shown in Table 1.

[0038] (Example 2) In Example 1 like Example 1 the outside which replaced the compound expressed above (5) with the compound expressed above (12) produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 1.

[0039] (Comparative example 1) In Example 1 not using the compound expressed above (5) like Example 1 the outside which did not combine coloring matter on said titanium oxide coating film produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 1.

[0040] (Comparative example 2) In Example 1 like Example 1 the outside which replaced with erythrosin B the compound expressed above (5) produced the optical semiconductor electrode and the photoelectric conversion device respectively produced the photoelectric conversion reaction and measured photoelectric current. The measurement result was shown in Table 1.

[0041]

[Table 1]

[0042]

[Effect of the Invention] According to this invention many problems in said former are solvable. According to this invention the optical semiconductor electrode photoelectric conversion device and the photoelectric conversion method of it being efficiently available and excelling in photoelectric conversion efficiency, stability, endurance etc. and manufacturing sunlight cheaply and easily can be provided.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is a section approximate account figure of the optical semiconductor electrode in Example 1.

[Drawing 2] Drawing 2 is an approximate account figure of the photoelectric conversion device of Example 1.

[Drawing 3] Drawing 3 is data in which the ultraviolet and visible absorption spectrum of the optical semiconductor electrode in Example 1 is shown.

[Description of Notations]

- 1 Optical semiconductor electrode
  - 2 Glass base material
  - 3 ITO layer
  - 4 Titanium oxide layer
  - 5 Pigment layer
  - 6 Adhesive agent
  - 7 Lead
  - 8 Glass tube
  - 9 Counterelectrode
  - 10 Contrast electrode
  - 11 Electrolytic solution
  - 12 Potentiostat
  - 13 Glass cell
-

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(54) 【発明の名称】 光半導体電極、光電変換装置及び光電変換方法

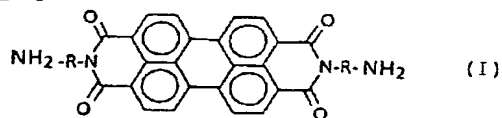
(57) 【要約】

【課題】 太陽光を効率的に利用可能でかつ光電変換効率、安定性、耐久性等に優れ、安価にかつ容易に製造し得る光半導体電極を提供すること。

【解決手段】 金属酸化物半導体の基材表面に、少なくとも下記一般式 (I) で表されるペリレン誘導体を吸着させた層を有することを特徴とする光半導体電極である。

一般式 (I)

【化1】



一般式 (I) 中、Rは、置換されていてもよい2価の炭化水素基又は複素環基を表す。

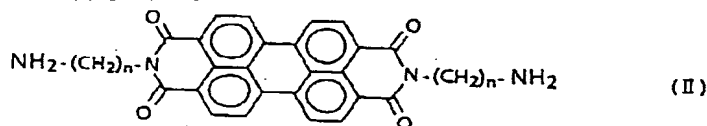
【0004】そこで、該光半導体の表面に、増感色素として、シアニン色素やキサンテン系色素等の有機色素や、トリス（2，2′-ビピリジル）ルテニウム（II）

錯体等の有機金属錯体を吸着させて分光増感させることが試みられており、変換効率の向上に有効な方法であることが知られている (T. Osa, M. Fujihira, Nature., 264, 349 (1976)、Brian O'Regan, Michael Gratzel, Nature, 353, 736 (1991)、特開平 1-220380 号公報等)。

【0005】しかしながら、シアニン色素やキサンテン系色素などの有機色素等は安定性、耐久性等の点で十分ではなく、一方、有機ルテニウム錯体などの有機金属錯体は変換効率、安定性等の面では優れているが、高価であるという問題がある。したがって、高効率・高耐久性でかつ安価な光電変換装置は未だ提供されていないのが現状である。

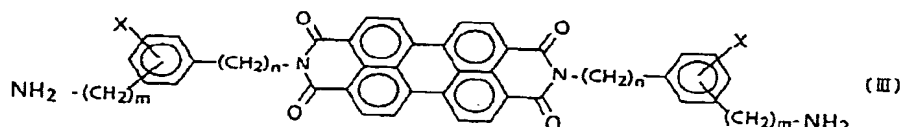
【0006】

【発明が解決しようとする課題】本発明は、前記従来における諸問題を解決し、以下の目的を達成することを課題とする。即ち、本発明は、太陽光を効率的に利用可能でかつ光電変換効率、安定性、耐久性等に優れ、安価にかつ容易に製造し得る光半導体電極、光電変換装置及び光電変換方法を提供することを目的とする。



【0011】一般式 (II) 中、n は、1～20 の整数を表す。

一般式 (III)



【0013】一般式 (III) 中、X は、水素原子、ハロゲン原子、 $-\text{CH}_3$ 、 $-\text{C}_2\text{H}_5$ 、 $-\text{OH}$ 、 $-\text{OCH}_3$ 、 $-\text{OC}_2\text{H}_5$ 、 $-\text{NH}_2$ 、 $-\text{COOH}$ 、又は  $-\text{NO}_2$  を表す。m 及び n は、各々 0～3 の整数を表す。

<3> 金属酸化物半導体が、酸化チタン、酸化スズ、酸化タングステン、酸化亜鉛、酸化インジウム、酸化ニオブ及びチタン酸ストロンチウムから選択される前記<1>又は<2>に記載の光半導体電極である。

<4> 金属酸化物半導体が、酸化チタンである前記<1>又は<2>に記載の光半導体電極である。

<5> 電解質溶液中に浸漬される一対の電極と、該一対の電極を通電可能に接続する接続手段とを少なくとも有してなり、該一対の電極の一方が前記<1>から<4>のいずれかに記載の光半導体電極であることを特徴とする光電変換装置である。

【0007】

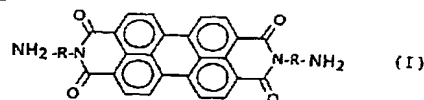
【課題を解決するための手段】

<1> 金属酸化物半導体の基材表面に、少なくとも下記一般式 (I) で表されるペリレン誘導体を吸着させた層を有することを特徴とする光半導体電極である。

一般式 (I)

【0008】

【化4】



【0009】一般式 (I) 中、R は、置換されていてもよい2価の炭化水素基又は複素環基を表す。

<2> 一般式 (I) で表されるペリレン誘導体が、下記一般式 (II) 及び (III) のいずれかで表される化合物である前記<1>に記載の光半導体電極である。一般式 (II)

【0010】

【化5】

【0012】

【化6】

<6> 互いに通電可能に接続された一対の電極を電解質溶液中に浸漬させ、該一対の電極の少なくとも一方に光を照射することにより光電変換反応を生じさせる光電変換方法において、前記光を照射する電極が前記<1>から<4>のいずれかに記載の光半導体電極であることを特徴とする光電変換方法である。

【0014】(光半導体電極) 本発明の光半導体電極は、金属酸化物半導体の基材表面に、少なくともペリレン誘導体を吸着させた層を有してなる。

【0015】金属酸化物半導体の基材ー前記金属酸化物半導体としては、例えば、酸化チタン、酸化スズ、酸化タングステン、酸化亜鉛、酸化インジウム、酸化ニオブ、チタン酸ストロンチウムなどが挙げられる。これらは1種単独で使用してもよいし、2種以上を併用してもよい。本発明においては、これらの中でも、特に光電変換特性、化学的安定性、製造容易性等の

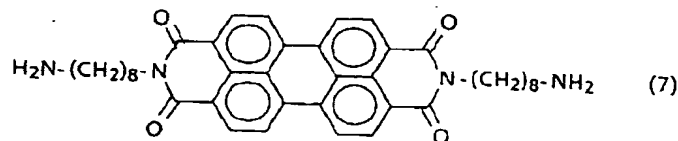
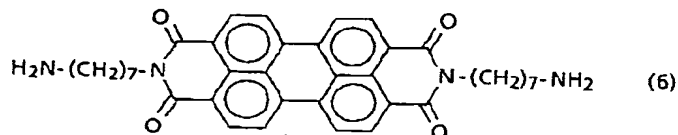
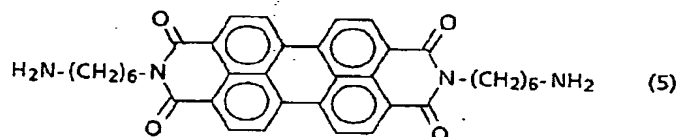
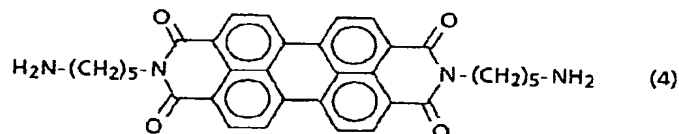
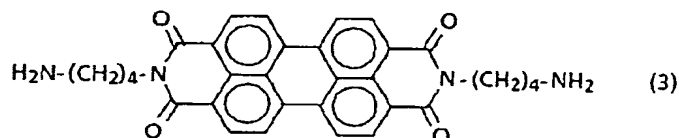
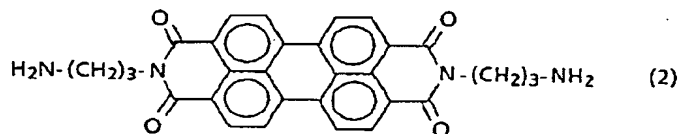
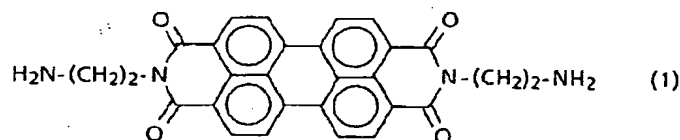
理由から、酸化チタンが好ましい。前記金属酸化物半導体の基材の形状、構造、大きさ等については特に制限はなく、目的に応じて適宜選択することができる。例えば、金属酸化物半導体のみからなる基材であってもよいし、ITOガラス、ネサガラス等による透明電極や白金、銅、黒鉛等による板状又はメッシュ状電極などの公知の電極上に金属酸化物半導体の被覆膜を形成してなる基材であってもよい。後者の基材の場合、該被覆膜は前記公知の電極上の全面に設けられていてもよいし、一部に設けられていてもよい。

#### 【0016】ーペリレン誘導体ー

本発明におけるペリレン誘導体としては、前記一般式(Ⅰ)で表されるものが好適に挙げられる。本発明においては、前記一般式(Ⅰ)で表されるペリレン誘導体の中でも、前記一般式(Ⅱ)及び(Ⅲ)のいずれかで表される化合物が好ましく、その中でも具体的には下記式(1)～(14)で表される化合物がより好ましい。

#### 【0017】

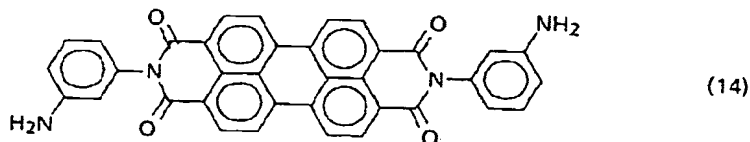
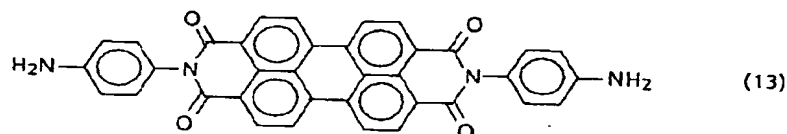
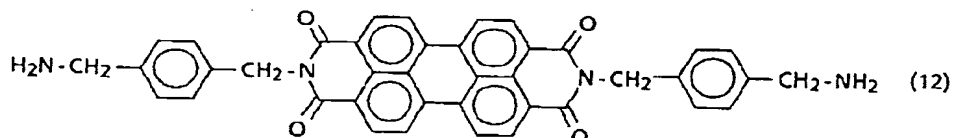
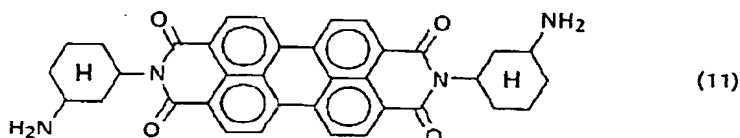
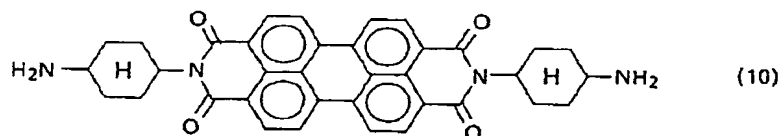
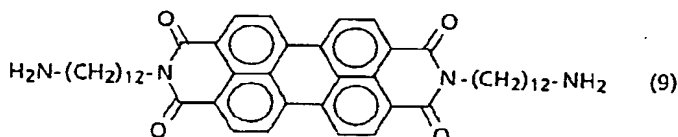
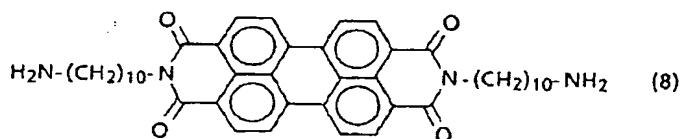
#### 【化7】



【0018】

【化8】





【0019】前記一般式(1)で示されるペリレン誘導体は、例えば、3, 4, 9, 10-ペリレンテトラカルボン酸無水物と、一般式、 $H_2N-R-NH_2$  で表されるジアミン化合物(式中、Rは、置換されていてもよい2価の炭化水素基又は複素環基を表す。)とを反応させることにより得られる。なお、前記反応に際しては、3, 4, 9, 10-ペリレンテトラカルボン酸無水物に対して、前記ジアミン化合物を少なくとも2当量(2当量以上)用いるが、ポリマー又はオリゴマーの副生を抑制するために、可能な限り過剰量用いるのが好ましく、一般に10当量以上用いるのが好ましい。

【0020】前記一般式(1)で表されるペリレン誘導体は、安価な原料を用いて容易に得られ、しかも化学的安定性、耐久性等に優れ、また、前記金属酸化物半導体の基材表面における保持性に優れ、光半導体電極を長期

間にわたり安定にかつ高効率に分光増感し得る。

【0021】(光半導体電極の作製)前記金属酸化物半導体の基材表面に、前記一般式(1)で表されるペリレン誘導体を吸着させた被覆膜を設ける工程は、該一般式(1)で表されるペリレン誘導体を酸性物質と共に溶媒に溶解した溶液中に、前記金属酸化物半導体の基材を浸漬することにより容易に達成される。

【0022】前記酸性物質としては、例えば、塩酸、硫酸、リン酸等の無機酸類や、酢酸、安息香酸、トリフルオロ酢酸、トルエンスルホン酸等の有機酸類など、前記一般式(1)で表されるペリレン誘導体と可溶性の塩を形成し得るものが挙げられる。これらは1種単独で使用してもよいし、2種以上を併用してもよい。これらの中でも、後述のアルコール系溶媒との組合せを考慮すると、酢酸が特に好ましい。

【0023】前記溶媒としては、例えば、メタノール、イソプロピルアルコール等のアルコール系溶媒、アセトン、メチルエチルケトン等のケトン系溶媒、ジメチルスルホキシド、N、N-ジメチルホルムアミド等の極性非プロトン性溶媒、水、これらの混合溶媒などが挙げられる。これらは1種単独で使用してもよいし、2種以上を併用してもよい。これらの中でも、アルコール系溶媒が特に好ましい。

【0024】なお、前記溶液中における前記一般式

(1)で表されるペリレン誘導体の含有量は、目的処理条件等に応じて適宜選択することができるが、前記溶媒100重量部に対して一般に0.01~1重量部程度である。また、前記溶液中における前記酸性物質の含有量は、前記金属酸化物半導体の基材の大きさ等により異なるため、目的に応じて適宜選択することができるが、前記ペリレン誘導体1モルに対し、少なくとも2モル当量以上必要であり、前記溶媒100重量部に対して一般に0.1~10重量部程度である。

【0025】前記浸漬は、室温で行ってもよく、あるいは吸着を促進するため必要に応じて前記溶媒の沸点以下の温度に加熱して行ってもよい。前記浸漬を行った後は、任意の溶媒、好ましくは水又はアルコール系溶媒を用いて、前記金属酸化物半導体の基材を洗浄し、乾燥することにより、表面に前記一般式(1)で表されるペリレン誘導体が吸着してなる層が形成された所望の光半導体電極が得られる。以上のようにして得られた本発明の光半導体電極は、以下の本発明の光電変換装置及び光電変換方法に好適に使用することができる。

【0026】(光電変換装置)本発明の光電変換装置は、電解質溶液中に浸漬される一対の電極と、該一対の電極を通電可能に接続する接続手段とを少なくとも有してなる。前記光電変換装置は、前記一対の電極と前記接続手段との外、目的に応じて適宜選択した機器等を備えていてもよい。

【0027】—一対の電極—

前記一対の電極における、一方は前記本発明の光半導体電極であり、他方は対向電極である。前記対向電極としては、電気化学的に安定なものであれば特に制限はなく、目的に応じて適宜公知のものから選択でき、例えば、白金、金、黒鉛等の板状電極、あるいはITOガラス、ネサガラス等の透明電極などから目的に応じて適宜選択することができる。

【0028】—接続手段—

前記接続手段としては、前記一対の電極を通電可能に接続し得る機能を有する限り特に制限はなく、目的に応じて適宜選択できるが、例えば、それ自体公知のリード線、各種金属、炭素、金属酸化物等の導電性材料からなる線材、板材、印刷膜、又は蒸着膜などが挙げられる。該接続手段は、前記一対の電極に通電可能に接続される。以上の本発明の光電変換装置は、以下の本発明の光

電変換方法に好適に用いることができる。

【0029】(光電変換方法)本発明の光電変換方法は、互いに通電可能に接続された一対の電極を電解質溶液に浸漬させ、該一対の電極の少なくとも一方に光を照射することにより光電変換反応を生じさせる。前記一対の電極における、光を照射される方は前記本発明の光半導体電極であり、他方は前記対向電極である。該一対の電極を通電可能に接続するには前記接続手段を用いることができる。このため、前記互いに通電可能に接続された一対の電極としては、前記本発明の光電変換装置を用いることができる。

【0030】—電解質溶液—

前記電解質溶液としては、特に制限はなく適宜選択することができるが、例えば、塩化カリウム、塩化リチウム、炭酸カリウム、過塩素酸テトラエチルアンモニウム等の塩類、水酸化ナトリウム、炭酸カリウム等のアルカリ類、硫酸、塩酸等の酸類、これらの混合物などの水溶液、あるいはアルコール、プロピレンカーボネートなどの非水溶媒溶液、などが挙げられる。これらは1種単独で使用してもよいし、2種以上を併用してもよい。また、本発明においては、光電流特性の安定化を図る目的で、更にヨウ化カリウム、p-ベンゾキノン等の可逆的に酸化還元反応を生ずるレドックス剤を前記電解質溶液に添加してもよい。

【0031】(光電変換反応)本発明の光電変換装置及び光電変換方法においては、以下のようにして光電変換反応を生じさせることができる。即ち、まず上述の一対の電極、即ち前記光半導体電極と前記対向電極とを前記電解質溶液中に浸漬する。次に、該光半導体電極に、300~650nmの波長域の単色光、該波長域におけるいずれかの帯域を包含する白色光又は多色光等を照射する。すると、該光半導体電極において光エネルギーが電気エネルギーに変換される。このとき、300~400nm未満の波長域の紫外光のみならず、400~650nmの波長域の可視光の光エネルギーまでも極めて効率よく電気エネルギーに変換される。

【0032】本発明においては、前記光半導体電極を用いることにより、酸化チタン等の金属酸化物単独では利用できない可視光までもが有効に利用でき、その結果、太陽光等の光の総合的な利用が可能となり、高い効率で太陽光等の光エネルギーを電気エネルギーに変換することができる。しかも、用いる前記光半導体電極においては、表面にペリレン誘導体の色素が強固に吸着し結合しているため、容易に該光半導体電極から脱離しないので、該光半導体電極の特性は長期間安定して維持でき、常に効率よく光電変換反応を行うことができる。

【0033】

【実施例】以下、本発明の実施例について説明するが、本発明はこれらの実施例に何ら限定されるものではない。

## 【0034】（実施例1）

## ー光半導体電極の作製ー

オルトチタン酸テトライソプロピル25mlを、純水150mlと濃硝酸1.54g（比重：1.38）との混合溶液中に、激しく攪拌しながら徐々に加えた。さらに攪拌を続けながら80℃に昇温し、同温度で8時間攪拌を続け、乳白色の安定な酸化チタンコロイド溶液を得た。このコロイド溶液を30mmHgの減圧下30℃で40mlまで濃縮し、酸化チタンコロイド溶液を調製した。前記酸化チタンコロイド溶液を、電極としてのITO／ガラス基材上にスピコート法でコーティングし、500℃で1時間焼成した。この操作を3回繰り返して、厚みが約1.0μmの酸化チタン被覆層を該ITO／ガラス基材上に形成した。得られた層の結晶構造をX線回折法により確認したところアナタース型とルチル型との混合物であることが確認された。前記酸化チタン被覆層が形成されたITO／ガラス基材を、N，N′-ビス（6′-アミノ-1′-ヘキシル）-3，4，9，10-ペリレンテトラカルボン酸ジイミド（前記（5）で表された化合物）100mg及び氷酢酸1mlをメタノール50mlに溶解した溶液に1時間浸漬した後、水で洗浄し、次いでメタノールで洗浄し、自然乾燥させた。

【0035】その後、酸化チタン膜の被覆されていないITO膜上にリード線7を接続し、基板端部及びリード線7の接続部をエポキシ樹脂で被覆し、図1に示すような光半導体電極を作製した。図1に示す光半導体電極1は、ガラス基材2上に、ITO層3、酸化チタン層4、及び、N，N′-ビス（6′-アミノ-1′-ヘキシル）-3，4，9，10-ペリレンテトラカルボン酸ジイミド（前記（5）で表された化合物）による色素層5をこの順に積層してなり、これらの積層面の端部及びリード線7との接続部は固着剤6としてのエポキシ樹脂で被覆され、固着されている。

## 【0036】ー光電変換装置の作製ー

図2に示すように、上記のように作製した光半導体電極1と、対向電極9として選択した白金電極と、参照電極10として選択した飽和カルメル電極とを透明なガラスセル13中の電解質溶液11に浸漬し、各々の電極を、接続手段としてリード線7を用いてポテンショスタット12に接続して、光電変換装置を作製した。前記電解質溶液11としては、0.1M硫酸ナトリウム／0.02Mヨウ化カリウム水溶液を用いた。なお、各々の電極にはリード線7が接続されており、通電可能になっている。リード線7は、ガラス管8内に収容されている。また、この光電変換装置には、参照電極10として飽和カルメル電極が通電可能に装備されている。以上により光電変換装置を作製した。

## 【0037】ー光電変換反応ー

以上により得られた光電変換装置において、前記光半導体電極の電位が前記参照電極に対して0Vになるように

保持して白色光（500Wのキセノンランプ、照度4000lux）又は550nmの単色光（1mW/cm<sup>2</sup>）を前記光半導体電極の裏側より照射した。この時生じた光電変換反応による光電流の値をポテンショスタットにより測定した。その測定結果を表1に示した。

【0038】（実施例2）実施例1において、前記（5）で表される化合物を前記（12）で表される化合物に代えた外は、実施例1と同様にして、光半導体電極、光電変換装置をそれぞれ作製し、光電変換反応を生じさせて光電流の測定を行った。その測定結果を表1に示した。

【0039】（比較例1）実施例1において、前記（5）で表される化合物を用いず、前記酸化チタン被覆膜上に色素を結合させなかった外は、実施例1と同様にして、光半導体電極、光電変換装置をそれぞれ作製し、光電変換反応を生じさせて光電流の測定を行った。その測定結果を表1に示した。

【0040】（比較例2）実施例1において、前記（5）で表される化合物をエリトロシンBに代えた外は実施例1と同様にして、光半導体電極、光電変換装置をそれぞれ作製し、光電変換反応を生じさせて光電流の測定を行った。その測定結果を表1に示した。

## 【0041】

【表1】

	初期		白色光連続照射(1h)後	
	白色光	550nm	白色光	550nm
実施例1	12.1μA	1.7μA	10.8μA	1.5μA
実施例2	13.0μA	1.8μA	11.7μA	1.7μA
比較例1	4.2μA	0.0μA	3.9μA	0.0μA
比較例2	13.8μA	1.7μA	4.7μA	0.1μA

## 【0042】

【発明の効果】本発明によると、前記従来における諸問題を解決することができる。また、本発明によると、太陽光を効率的に利用可能でかつ光電変換効率、安定性、耐久性等に優れ、安価にかつ容易に製造し得る光半導体電極、光電変換装置及び光電変換方法を提供することができる。

## 【図面の簡単な説明】

【図1】図1は、実施例1における光半導体電極の断面概略説明図である。

【図2】図2は、実施例1の光電変換装置の概略説明図である。

【図3】図3は、実施例1における光半導体電極の紫外可視吸収スペクトルを示すデータである。

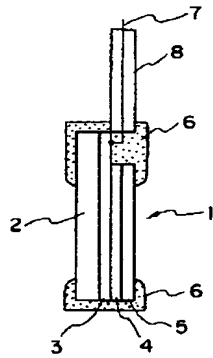
## 【符号の説明】

- 1 光半導体電極
- 2 ガラス基材
- 3 ITO層
- 4 酸化チタン層
- 5 色素層

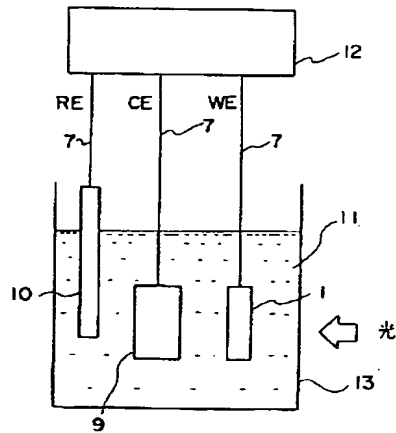
- 6 固着剤
- 7 リード線
- 8 ガラス管
- 9 対向電極

- 10 対照電極
- 11 電解質溶液
- 12 ポテンシオスタット
- 13 ガラスセル

【図1】



【図2】



【図3】

